Identification of nanocrystalline goethite in reduced clay formations: Application to the Callovian-Oxfordian formation of Bure (France)

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ABSTRACT

The Callovian-Oxfordian (COx) clay formation in the Paris Basin (France) has been the target of many studies investigating the feasibility of deep nuclear waste disposal in a reduced clay formation. To determine the mobility of radionuclides in the host rock formation, modeling of the porewater chemistry, particularly iron solute concentrations, is necessary. Notably, this study aims to understand the supersaturation of Fe(III) oxyhydroxides given by models. Fe(III) oxyhydroxides have been identified magnetically in unpreserved Callovian-Oxfordian samples. In this study, a set of magnetic measurements are used to detect the Fe-bearing magnetic minerals present in the COx clay formation. A core sample from the borehole FOR1118, preserved from air since its collection, is the target of this study. The magnetic measurements performed show that magnetite and goethite are the main magnetic minerals (<0.2%), together with probable greigite, and occur in low concentrations. Goethite occurs as nanoparticles dispersed in the clayey matrix, and not enclosed in other minerals or in organic matter. It is unlikely that the goethite is an alteration by-product, as particular care was undertaken. This finding resolves the discrepancies between observations and previous modeling results.

Keywords: Goethite, nanoparticles, Callovian-Oxfordian clay formation, Paris Basin

INTRODUCTION

The Underground Research Laboratory (URL) built in the Callovian-Oxfordian Clay Formation (COx) in Bure, France, is an experimental site used by the French National Radioactive Waste Management Agency (Andra) to test the feasibility of deep nuclear waste disposal in a reduced clay formation. To assess the durability of materials (e.g., glass, stainless steel, concrete, engineered clay barrier), and to determine the speciation and related mobility of the radionuclides in the host rock formation, it is necessary to model the chemistry of the clay porewater (e.g., Gaucher et al. 2009). Porewater composition models still have some deficiencies that need to be addressed. One of the most problematic issues is the understanding and modeling of iron (Fe) solute concentrations and the subsequent understanding of redox conditions in the formation. This information is mandatory for robust blind simulation modeling of redox perturbations in reduced clay formations (e.g., migration of redox sensitive radionuclides). For instance, predicted water compositions are supersaturated with respect to Fe(III) oxy(hydr)oxides (Gaucher et al. 2009). To date, all of the various microscopic and spectrometric techniques used on very well-preserved samples of COx clay in liquid nitrogen failed to predict the presence of Fe oxy(hydr)oxides (Tourannas et al. 2008; Lerouge et al. 2011). This inconsistency between observations and modeling could result from (1) a concentration of Fe(III) oxy(hydr)oxides that is too low to be detected by the different techniques or (2) a problem with the model.

This study aims to test the first hypothesis using a rock magnetic approach to detect the magnetic minerals (e.g., iron oxides, oxyhydroxides) possibly present in the reduced clay-rich formation. The main approach used in this paper is based on low-temperature magnetic measurements (from 10 to 400 K). It is non-destructive and allows the identification of magnetic minerals, even if they occur in very low concentrations on the order of parts per million per volume (ppmv) to parts per billion per volume (ppbv).

ROCK MAGNETISM IN CALLOVIAN-ORDOXFORDIAN FORMATION: A BRIEF REVIEW

Diamagnetism is a property of all magnetizable minerals. However, diamagnetism is overshadowed if any other forms of magnetism are present (paramagnetism, ferromagnetism). When a mineral is subjected to a magnetic field (H), it acquires an induced magnetization, M, that is the sum of the transient and remanent magnetizations contributions. Only the ferromagnetic (sensu lato) minerals can retain a remanence. The magnetic susceptibility, χ = M/H, measured at room temperature under a weak magnetic field, is expressed as: χ = χ_diam + χ_para + χ_ferro. In argillaceous rocks, χ_dia is ~14 μSI (Hrouda 1986). χ_para is similar to χ_ferro depending on the ratio of clays (χ_para) and ferromagnetic minerals (χ_ferro). In the Callovian-Oxfordian Bure claystones, χ is dominated by the paramagnetic contribution (χ_para) and a positive correlation exists between the magnetic susceptibility and the